FULL PAPER

Enhanced Penta(organo)[60]fullerenes by electroactive donor units for supramolecular polymers

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Abstract: New penta(organo)fullerenes donor-acceptor systems bearing five recognition units have been prepared in order to promote their self-assemblies in solution and in solid state. The host-cavity formed due to the perfect organization of the electro and/or photoactive units around the fullerene, together with the π-π and electronic interactions led to supramolecular arrangement similar to shuttlecocks nested into each other.

Introduction

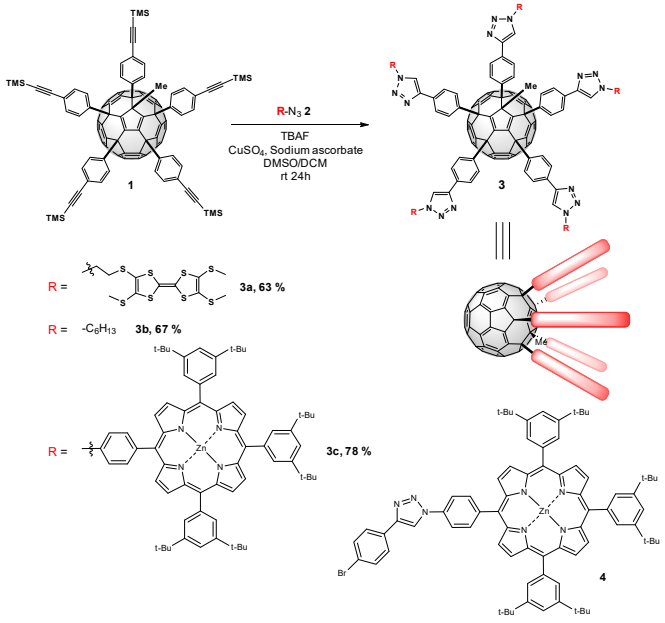
Nowadays, supramolecular chemistry continues its expansion paying special attention to understand the biological processes, self-assembly, molecular recognition, catalysis and to build new functional materials.[1] In this context, fullerene-based supramolecular assemblies have been investigated since the two last decades.[2] Thus, interesting materials with fullerene-containing supramolecular polymers[3] have been developed using different supramolecular organizations depending on the nature of their assemblies (hydrogen bond,[4] hydrophobic,[5] metal-ligand,[6] aromatic π-π stacking[7]…).

Supramolecular polymers based on fullerene C_{60} have been particularly investigated using monoadducts monomers.[8] But studies of polyadducts[9] exhibiting an intrinsic multivalent effect have been less developed. Among the latter, pentafullerenes described by Nakamura and coworkers, obtained by a regioselective pentafunctionnalization reaction to C_{60}, showed a conical structure formed by five units.[10] Such resulting cavity could lead to supramolecular self-assemblies by intermolecular complexation of C_{60}. To the best of our knowledge, properties of penta(organo)fullerenes have been studied with benzene rings,[11] aryl chains of different lengths[12] or the proton interchange contained in the cavity.[13] Functional electro- or photoactive units have not been yet reported.

We recently described donor-acceptor supramolecular polymers based on penta(organo)[60]fullerenes by introducing five donor tetrathiafulvalene (TTF) fragments as electroactive recognizing units leading to a host-cavity complementary to fullerene C_{60} acceptor.[14] In this full research paper, we present the influence of the donor unit on the self-assembly of these materials through supramolecular nesting organization. The contribution of π-π interactions in the formation of aggregates will be also discussed. These studies of self-assembly are supported by NMR, electrochemical analyses, mass spectrometry and microscopies (TEM and AFM).

Results and Discussion

The synthetic strategy of penta(organo)[60]fullerenes is based on five straightforward 1,3-dipolar cycloadditions taking place simultaneously using penta(TMS)[60]fullerene derivative **1** leading to monomers **3a-c** (Scheme 1). Compound **1** was synthesized by a regioselective five-fold addition of 4-substituted phenyl cuprate reagent to [60]fullerene.[15] From the latter, the different fragments were introduced in a single step through five simultaneous 1,3-dipolar cycloadditions using copper-catalyzed "click chemistry" reactions using corresponding azidoTTF **2a**,[16] azidohexyl **2b**[17] and azidoporphyrin building block **2c**[18]. Target penta[60]fullerenes **3a**, **3b** and **3c** were obtained in 63%, 67% and 78% yields, respectively. Note that the terminal alkyne deprotections of **1**, allowing reaction with the corresponding azido compound, was generated in situ.[19] Compound **4** was synthesized as reference for further studies following the same procedure but from 4-bromoethynylbenzene[12a].



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Scheme 1. Synthesis of penta(organo)[60]fullerenes **3a, 3b** and **3c** and reference compound **4**.

HPLC studies revealed the high purity of the synthesized penta(organo)[60]fullerenes **3a-c** (see SI Figure S1). Molecular structures of **3a-c** and **4** were confirmed by NMR spectroscopy (^{1}H and ^{13}C) (see SI Figures S2-S12) and mass spectrometry (MALDI-TOF). TGA analyses were carried out to prove the thermal stability in the solid state of penta(organo)[60]fullerene derivatives **3a, 3b, 3c** and **4**, respectively. All of them have shown to be stable up to 110 °C where a weight loss of 4%, 2.5%, 3% and 4% for **3a**, **3b**, **3c**, and **4** respectively, is observed due to the N_2 extrusion from the triazole rings. A second loss corresponding to the degradation of the five units attached to the fullerene cage appears at 245 °C for **3a**, 300°C for **3b** and 365 °C for **3c** (see SI Figure S13).

As expected based on our previous studies, using penta(organoTTF)[60]fullerene **3a**, we have obtained donor-acceptor systems possessing a host-cavity complementary to fullerene, making possible their self-assemblies which were demonstrated by NMR spectroscopy, mass spectrometry (MALDI-TOF), electrochemical studies, Transmission Electron Microscopy (TEM), and Atomic Force Microscopy (AFM) (see SI Figures S14-S18). Based on these results we wanted to go one step further and in order to evaluate the role of benzene and triazole rings in the supramolecular π-π interactions involved in the formation of aggregates, we have studied the self-assembly ability of penta(hexyl)[60]fullerene **3b** bearing a non electroactive hexyl group.

The supramolecular assembly behavior of **3b** was first investigated by recording ^{1}H-NMR spectra at different concentrations between 0.3 and 20 mM ($CDCl_3$, 25 °C) (Figure 1). At high concentrations, the signals of the aromatic groups showed an *upfield* shift thus suggesting the formation of aggregates. However, the observed upfield shift (0.02 ppm) appears not significant and is much lower than the one observed in case of monomer **3a** (0.4 ppm). Therefore, it seems that both benzene and triazole rings are involved through π-π interactions in the aggregate formation. However, the donor-acceptor interaction may be the predominant one.

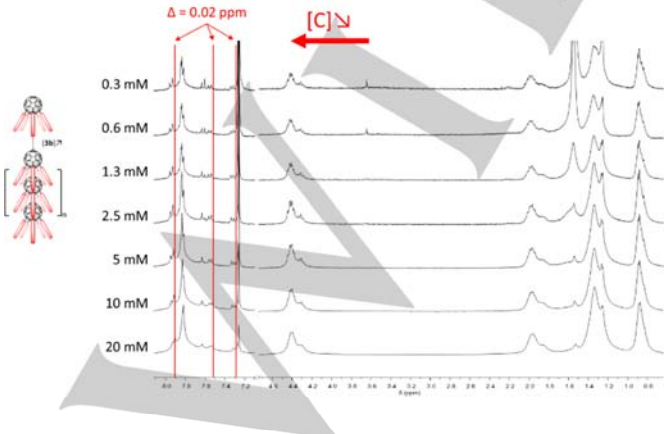

Figure 1. ^{1}H-NMR spectra of **3b** at different concentrations (0.3-20 mM) in $CDCl_3$ at 25 °C.

The lower participation of π-π versus donor-acceptor interactions in the supramolecular recognition process has been confirmed by ^{1}H DOSY NMR of **3b** carried out at different concentrations between 1.3 and 40 mM. Upon concentration of **3b**, no significant decrease of the diffusion coefficient values was observed (see SI Figure S19). MALDI-TOF mass analysis confirmed also the weakness of the π-π interactions in the self-assembly capability of penta(hexyl)[60]fullerene **3b**, because mass spectra only showed the peak corresponding to the monomer at m/z = 1876.2 (see SI Figure S20). No signal related to higher weight supramolecular aggregates was observed.

Additionally, Transmission Electron Microscopy (TEM) and Atomic Force Microscopy (AFM) were performed to study the possible supramolecular aggregates of **3b** in the solid state (Figure 2). TEM images displayed the presence of spherical aggregates with diameters between 4-9 nm that may match 2-4 units of monomer **3b**. The topographic AFM images at 50 µM showed aggregates scattered over the surface with different sizes. An example of the observed aggregates is given in figure 2. The corresponding profile of the displayed AFM image shows that this aggregate is composed of several smaller clusters with heights ranging from 3 to 6 nm which are in good agreement with the observed sizes by TEM (see SI Figure S21). We can thus presume that the penta(hexyl)[60]fullerene **3b** exhibits an organization within the monodispersed spherical clusters that merge to form larger polydispersed aggregates.

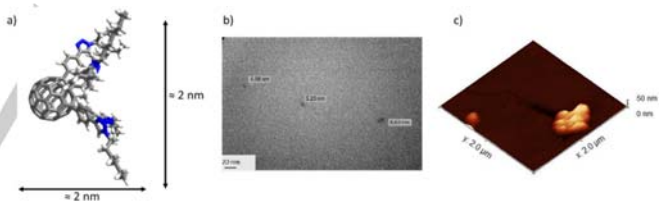

Figure 2. a) Structure representation of monomer **3b**; b) TEM images of the supramolecular organization of **3b** at 50 µM in PMMA matrix; c) 3D AFM topography image of **3b** at 50 µM.

^{1}H NMR studies, AFM and TEM images of penta(hexyl)[60]fullerene **3b** confirmed the role of the phenyl-triazole in self-assemblies through π-π interactions, while the studies carried out with penta(TTF)[60]fullerene **3a** proved the relevance of electronic interactions. To get a better understanding of self-assembly, a third penta[60]fullerene **3c** bearing five Zn-porphyrin recognition units was investigated.

The first evidence of formation of aggregates with **3c** was obtained by ^{1}H-NMR studies at different concentrations between 0.3 and 10 mM ($CDCl_3$, 25 °C) (Figure 3). In fact, all signals are broad with an increase of the monomer concentration. Particularly a downfield shift of signals in the aromatic region and those of *tert*-butyl groups was observed. For a rigorous

comparison, the same analysis was carried out using reference **4** (see SI Figure S22) and no significant change could be detected.

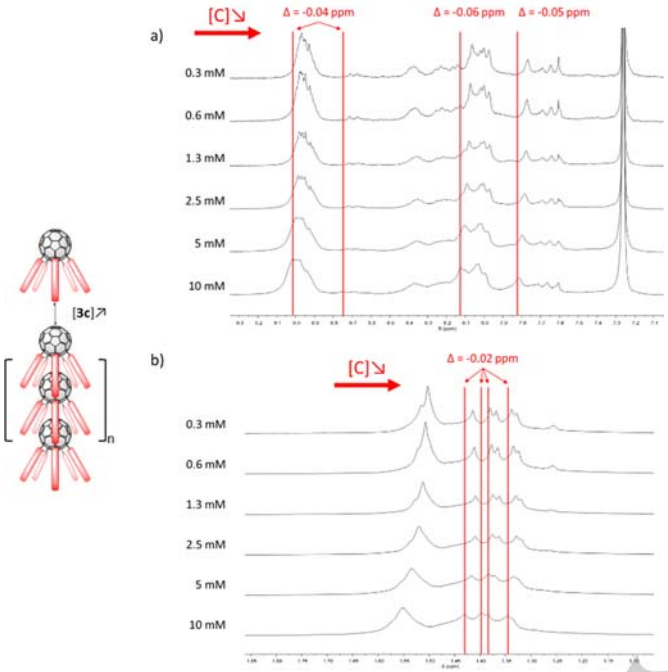

Figure 3. ^{1}H-NMR spectra of **3c** at different concentrations (0.3-10 mM) in $CDCl_3$ at 25 °C.

The formation of aggregates was further supported by the self-diffusion coefficients (D) of **3c** at 1.3, 2.5, 5, 10 and 15 mM in $CDCl_3$ obtained from ^{1}H DOSY NMR experiments (Figure 4). The decrease of the diffusion coefficient values found upon **3c** concentration (D(1.3 mM)= $2.34x10^{-10}$, D(2.5 mM)= $2.15x10^{-10}$, D(5 mM)= $1.84x10^{-10}$, D(10 mM)= $1.54x10^{-10}$ and D(13 mM)= $1.38x10^{-10}$ m^2/s) is in agreement with formation of supramolecular aggregates[20] by encapsulation of C_{60} within the conical host cavity of another molecule.

An estimated molecular weight (MW) has been calculated from the Morris equation (T = 298 K) for these supramolecular aggregates[21] (Table 1). As expected, these results indicated that the aggregate is larger when increasing the monomer concentration. Moreover, the corresponding size at 15 mM is compatible with the oligomeric formation containing up to seven monomers.

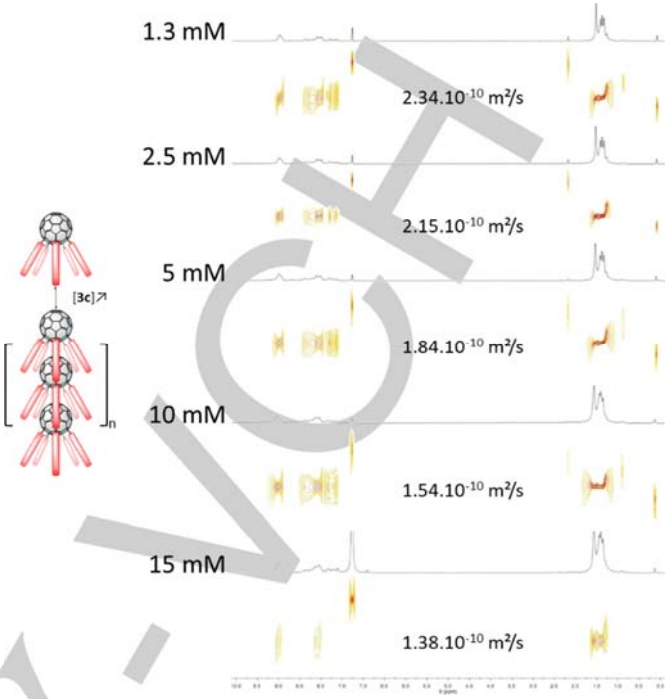

Figure 4. ^{1}H DOSY NMR spectra (300 MHz, $CDCl_3$, 25°C) of **3c** at different concentrations.

Table 1. Molecular weight (MW) estimated from the Morris equation for ^{1}H DOSY NMR of **3c** at different concentrations.

Concentration (mM)	D ($m^2.s^{-1}$)	MW ($g.mol^{-1}$)	Number of monomers **3c**[a]
1.3	2.34	11725	1.8
2.5	2.15	14699	2.2
5	1.84	22179	3.4
10	1.54	35486	5.4
15	1.38	47810	7.3

[a] MW of monomer **3c** 6520.05 $g.mol^{-1}$.

Electrochemical properties of penta(Zn-porphyrin)[60]fullerene **3c** were determined by cyclic voltammetry. The experiments were performed at room temperature in *o*-DCB/MeCN (4/1). Figure 5 shows the cyclic voltammogram of **3c** at 0.8, 1.0, 2.5, 5.0 and 10 mM. The voltammogram of **3c** showed two oxidation waves at 0.28 and 0.60 V vs. Fc/Fc^+ corresponding to the successive generation of cation radical and dication species on each Zn-porphyrin framework are observed. The redox potentials are similar for the five porphyrin moieties thus indicating that no electronic interaction was occurring between porphyrin units. Processes at - 2.18 and - 2.37 V vs. Fc/Fc^+ correspond to the reduction of Zn-porphyrin into radical anion and dianion, respectively. The reduction wave at – 1.53 V vs. Fc/Fc^+ could be

attributed to the azide fragment.[22] The electron reduction waves corresponding to the C_{60} fragment are masked by reduction waves of the five electroactive units.

Both reduction and oxidation waves are shifted towards more energetic processes by an increase of penta(Zn-porphyrin)[60]fullerene **3c** concentration. Such changes must be related to the existence of electronic communication between C_{60} and porphyrin units as a result of their assembly in solution.

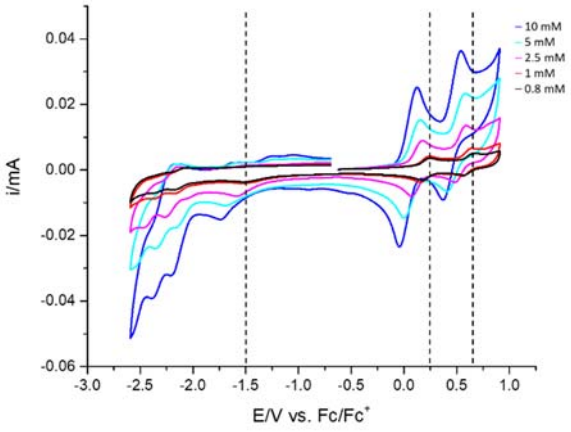

Figure 5. Cyclic voltammograms of **3c** at different concentrations: 0.8, 1.0, 2.5, 5.0 and 10 mM (V vs Fc/Fc^+; GCE as working electrode; Bu_4NPF_6 0.1 M, 100 mV/s, *o*-DCB/MeCN 4/1; 298K).

MALDI-TOF mass analysis confirmed the self-assembly capability of the penta(Zn-porphyrin)[60]fullerene **3c**. Mass spectrum showed not only the peaks of the monomer (at m/z = 6618.8) but also signals corresponding to higher weight supramolecular aggregates such as dimers and trimers (Figure 6).

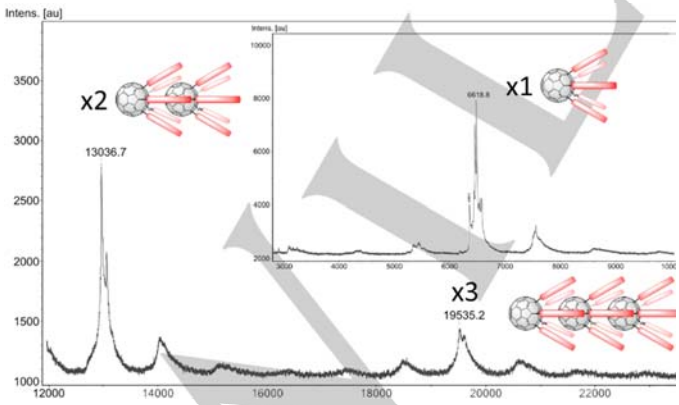

Figure 6. MALDI-TOF spectrum of **3c**.

Transmission Electron Microscopy (TEM) was carried out to study the self-assembly capability in the solid state. The samples were prepared with penta(Zn-porphyrin)[60]fullerene **3c** at two different concentrations (25 and 50 µM) and embedded in a poly(methylmethacrylate) (PMMA) matrix (Figure 7 and S22). The postulated head-to-tail organization is highlighted in Figure 7. We effectively observed linear chains of spherical arrangements of lengths between 55 and 1600 nm. The wideness of these aggregates is about 5 nm that matches the size of the monomeric unit of **3c** according to the scheme of the molecule represented in figure 8. As result, the observed linear structures correspond to the assembly of 18-500 units of monomer **3c,** assuming a size of 5 nm**.** Consequently, the observed supramolecular structure suggested the coalescence of a large number of monomers according to a self-assembly mechanism allowing then linear organization.[23]

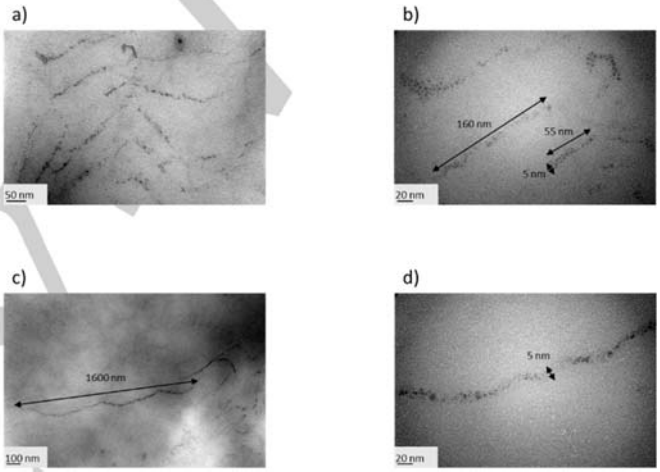

Figure 7. TEM images of the supramolecular organization of **3c** at 50 µM in PMMA matrix, a) scale 50 nm, c) scale 100 nm, b) and d) scale 20 nm.

Additionally, Atomic Force Microscopy (AFM) studies were carried out using a solution of **3c** (25 µM) in chloroform which was drop-casted onto glass substrate. The topographic images at 10 µm (Figure 8) show a smooth homogeneous surface with an average roughness of 1.5 nm. When zooming, small spherical clusters are observed (Figure 9). From the profile given, we can extract a cluster height ranging from 2 nm to 5 nm. In addition, these clusters are ordered to form a quasi-linear assembly whose length, in the present case, is 1.25 µm. This is in very good agreement with the TEM observations, and confirm the nesting of several penta(Zn-Porphyrin)[60]fullerene monomers. On the contrary, reference **4** show any nanostructure under the same conditions (see SI Figure S24).

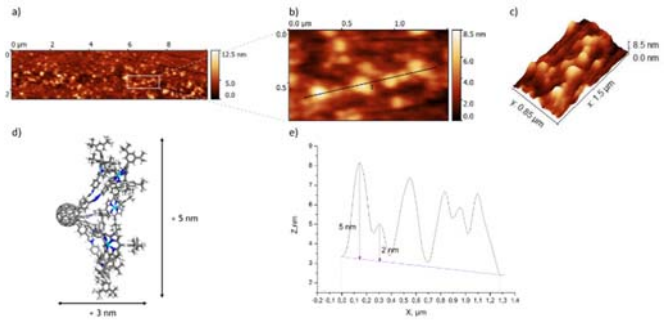

Figure 8. a) AFM images of **3c** at 25µM; b) 2D representation of **3c** at 25 µM extracted from the insert; c) 3D representation of **3c** at 25 µM extracted from the insert; d) structure representation of monomer **3c**; e) related profile of **3c** extracted from the insert.

Conclusions

In summary, we have developed new donor-acceptor systems based on penta(organo)[60]fullerene enhanced with electro- and/or photoactive fragments (TTF or ZnP). Studies of these systems have demonstrated their ability to build supramolecular self-assembled polymers suggesting the formation of shuttlecocks by nesting monomers one into each other. These materials were shown to be accessible thanks to the conical host-cavity created around the fullerene and involving predominantly donor-acceptor interactions. Large aggregates could be also observed both in solution with a strong dependence of the concentration and in solid state. Applications in optoelectronic devices are currently under investigation using these fullerene-based supramolecular donor-acceptor polymers.

Experimental Section

General procedure for synthesis of penta(organo)[60]fullerene **3**.

To a solution of compound **1**[15a] (56 µmol), freshly prepared azidocompound **2** (0.6 mmol), $CuSO_4.5H_2O$ (3 µmol) and sodium ascorbate (14 µmol) in DMSO (2 mL) and CH_2Cl_2 (2 mL) was added TBAF (1 M in THF, 1.13 mL, 1.13 mmol). The mixture was stirred at room temperature for 24 h. Then, the solution was diluted with $CHCl_3$ (100 mL), washed with water (3 x 100 mL), dried over $MgSO_4$, filtered and concentrated under vacuum. The crude was purified by gel chromatography (SiO_2, $CHCl_3$ followed by 2% v/v MeOH in $CHCl_3$) and the solvent was removed under vacuum. The product was washed three times by centrifugation with acetonitrile to obtain desired compound **3**.

Compound **3a**: brown solid, 63%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.03 (s, 2H), 7.97 (s, 2H), 7.93 (s, 1H), 7.91 – 7.80 (m, 8H), 7.75 – 7.59 (m, 10H), 7.53 (d, *J* = 8.2 Hz, 2H), 5.44 (s, 1H), 4.70 – 4.53 (m, 10H), 3.38 – 3.21 (m, 10H), 2.49 – 2.30 (m, 45H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.9, 152.9, 148.7, 148.5, 148.3, 148.1, 147.8, 147.0, 146.9, 146.0, 145.9, 145.7, 145.4, 144.8, 144.5, 144.4, 144.3, 143.3, 139.6, 133.9, 133.8, 130.3, 130.0, 128.9, 128.6, 128.3, 127.6, 127.5, 126.4, 126.2, 121.2, 121.0, 112.8, 109.6, 78.0, 77.4, 60.9, 58.9, 58.8, 49.7, 35.9, 29.8, 19.4 ppm. MS (MALDI-TOF +): calcd. for $C_{156}H_{91}S_{40}N_{15}$: 3440.6 $[M]^+$, found 3439.8. HPLC analysis: retention time: 3.05 min (eluent: toluene, flow rate: 1 mL/min, wavelength: 320 nm).

Compound **3b**: orange solid, 67%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.00 – 7.69 (m, 20H), 7.63 (s, 1H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 4.60 – 4.12 (m, 10H), 2.00 – 1.94 (m, 10H), 1.48 – 1.13 (m, 33H), 0.90 – 0.86 (m, 15H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.5, 157.0, 152.9, 151.8, 148.8, 148.7, 148.5, 148.4, 148.3, 148.2, 147.9, 147.7, 147.4, 147.3, 147.2, 147.1, 146.9, 145.7, 145.5, 144.9, 144.5, 144.4, 144.35, 144.3, 144.2, 143.9, 143.8, 142.9, 142.6, 142.4, 139.5, 137.8, 130.6, 130.4, 129.5, 129.3, 129.1, 128.8, 126.4, 126.2, 126.1, 125.6, 120.2, 120.1, 119.7, 62.6, 62.4, 61.0, 58.2, 50.7, 50.6, 50.5, 31.3, 31.25, 31.2, 31.1, 30.5, 30.4, 30.3, 29.9, 29.8, 29.7, 26.4, 26.3, 26.2, 22.8, 22.6, 22.5, 22.4, 14.3, 14.1, 14.0 ppm. MS (MALDI-TOF +): calcd. for $C_{131}H_{93}N_{15}$: 1877.3 $[M]^+$, found 1876.2. HPLC analysis: retention time: 3.11 min (eluent: toluene, flow rate: 1 mL/min, wavelength: 320 nm).

Compound **3c**: purple solid, 78%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.08 – 8.82 (m, 40H), 8.72 (s, 2H), 8.67 (s, 2H), 8.46 – 7.89 (m, 61H), 7.87 – 7.53 (m, 25H), 1.62 – 1.20 (m, 273H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.7, 150.6, 150.5, 149.8, 148.7, 148.6, 148.5, 144.1, 141.9, 136.5, 135.5, 132.7, 132.5, 131.3, 129.8, 129.5, 129.2, 128.3, 126.5, 123.0, 122.8, 120.9, 118.9, 118.6, 35.2, 35.1, 35.05, 35.0, 31.9, 31.85, 31.8, 31.7, 29.9, 29.5, 22.9, 14.3 ppm. MS (MALDI-TOF -): calcd. for $C_{441}H_{403}N_{35}Zn_5$: 6507.9 $[M]^-$, found 6618.8. HPLC analysis: retention time: 2.93 min (eluent: toluene, flow rate: 1 mL/min, wavelength: 425 nm).

Synthesis of reference compound **4**:

To a solution of (4-bromophenylethynyl)trimethylsilane[11a] (46 mg, 0.18 mmol) and freshly prepared **2c**[17] (95 mg, 0.09 mmol) in a mixture of DMSO (3 mL) and CH_2Cl_2 (3 mL) were added $CuSO_4.5H_2O$ (1 mg, 4 µmol) and sodium ascorbate (5 mg, 25 µmol). Then TBAF (1 M in THF, 900 µL, 0.9 mmol) was added and the solution was stirred at room temperature for 24 h. The solution was subsequently diluted with CH_2Cl_2, washed with water (3 x 100 mL). After drying the organic phase over $MgSO_4$ and filtration, the solution was concentrated under vacuum. The crude was purified by gel chromatography (SiO_2, $CHCl_3$) to obtain the desired compound as a purple solid (64 mg, 58%). ^{1}H NMR (300 MHz, $CDCl_3$): 9.10 – 9.00 (m, 6H), 8.96 (d, *J* = 4.6 Hz, 2H), 8.51 (s, 1H), 8.43 (d, *J* = 8.1 Hz, 2H), 8.19 (d, *J* = 8.1 Hz, 2H), 8.13 – 8.04 (m, 6H), 7.92 (d, *J* = 8.2 Hz, 2H), 7.84 – 7.75 (m, 3H), 7.67 (d, *J* = 8.2 Hz, 2H), 1.53 (s, 54H) ppm. ^{13}C NMR (75 MHz, THF-d_8): δ 151.5, 151.4, 151.3, 150.8, 149.5, 149.4, 148.15, 145.2, 143.8, 137.8, 136.4, 133.0, 132.9, 132.7, 132.6, 131.8, 131.5, 130.7, 130.5, 128.4, 123.0, 122.8, 122.7, 121.7, 119.7, 119.4, 118.9, 35.8, 32.2 ppm. HRMS (FAB +): calcd. for $C_{76}H_{80}BrN_7Zn$: 1233.4955 $[M]^+$, found 1233.4950.

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Keywords: Supramolecular polymer, Self-assembly, Fullerene, Donor-acceptor system, Supramolecular recognition

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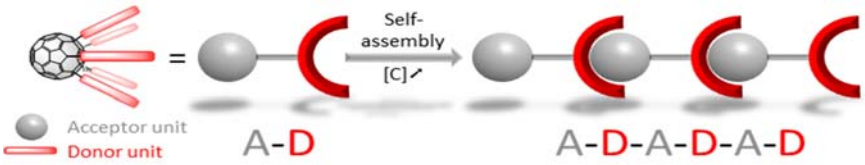
Host-Guest systems

FULL PAPER



Electroactive shuttlecocks fullerenes**:** Conical host-cavity created around the fullerene by five electro and/or photoactive units promote self-assemblies similar to shuttlecocks nested into each other with the π-π and electronic interactions.

*Antoine Busseau, Carmen Villegas, Sylvie Dabos-Seignon, Piétrick Hudhomme and Stéphanie Legoupy**

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Enhanced Penta(organo)[60]fullerenes by electroactive donor units for supramolecular polymers